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Interim Report
I-B2119-1

Technical Report

LIQUID METAL EMBRITTLEMENT

by

Richard W. Vook

August 1965

Sponsored by

OFFICE OF NAVAL RESEARCH

ONR Contract Number Nonr-4225(00)

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THE FRANKLIN INSTITUTE RESEARCH LABORATORIES

BENJAMIN FRANKLIN PARKWAY AT 20TH STREET, PHILA. 3, PA.

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LIQUID METAL EMBRITTLEMENT

1. INTRODUCTION

A recent paper* summarized the results of our electron microscope investigations of liquid metal embrittlement in the solid Cu - liquid Bi system. In the present paper further observations illustrating some of the points made in the earlier work are presented. In addition some new results of an investigation of the Zn-Hg system are included. These results show that mercury tends to flow preferentially along the intersections of slip planes and the surface of the foil and in the slip direction. Dissolution phenomena similar to those observed in the Cu-Bi system were observed also in the Zn-Hg and α-brass mercury system. Only a few observations have been made in the latter case.

2. DISCUSSION

Solid Cu-Liquid Bi System

Figure 1 illustrates the progressive accumulation of liquid bismuth at the intersection with the surface of the foil of a grain boundary in annealed copper. The successive electron micrographs show the gradual thinning at T due to dissolution of the foil. The first hole to form occurred along the grain boundary at H after tension had been applied to the sample. Increasing tension caused the crack to propagate sideways along the grain boundary.

The specimen in Figure 2 was prepared from a copper foil annealed at 500°C for two hours. At room temperature a 200Å bismuth film was deposited on one side of it. The bismuth evaporation was followed by the vapor deposition of a thin SiO film on top of the bismuth film. Consequently the bismuth was

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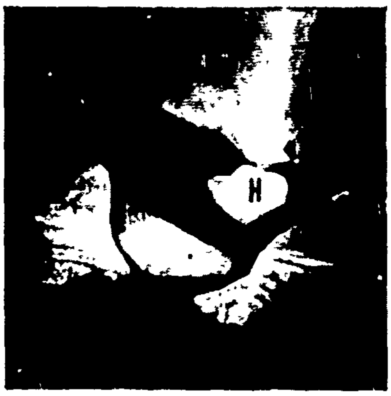
*See appendix for the text of this paper.

(a)

(b)

(c)

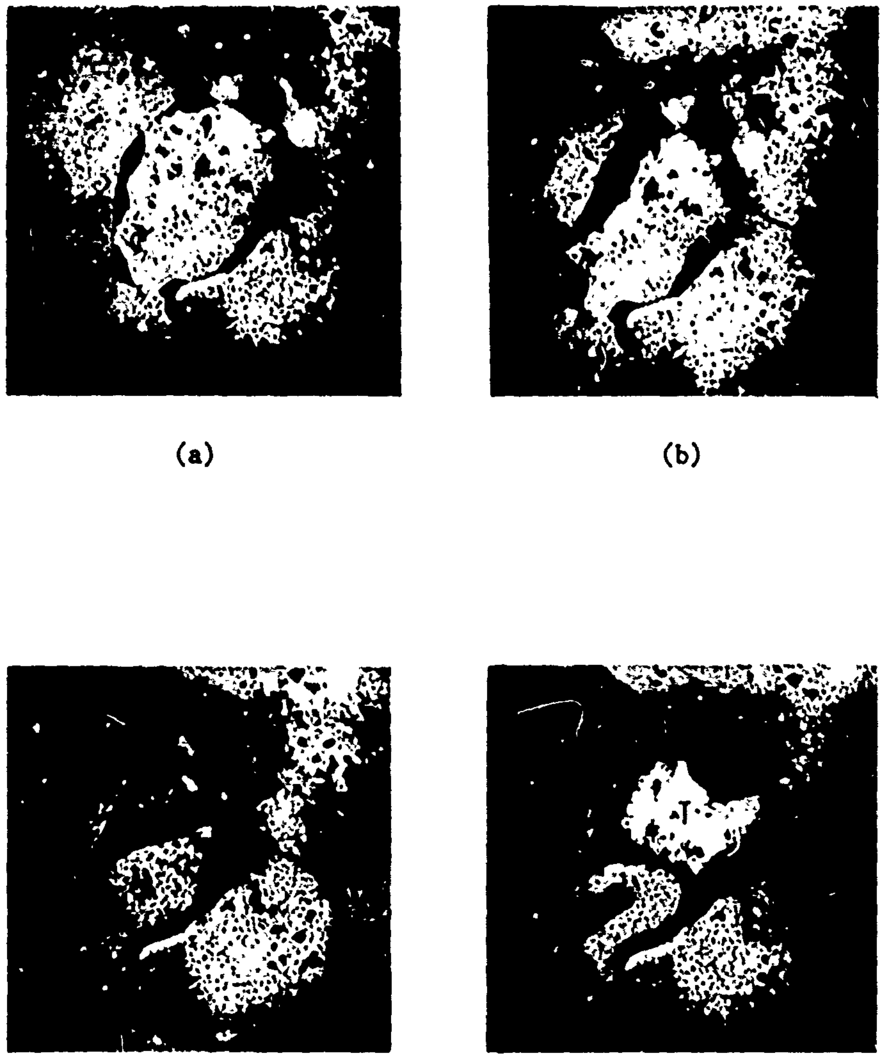
(d)



(e)

(f)

Fig. 1 - Flow and concentration of liquid bismuth B at a grain boundary G in annealed copper. Tension was applied after a, d, and e were taken. In c., T indicates a thin area. In d two pools of bismuth have joined. In e., H indicates a hole in the film. Further propagation of the fracture is shown in f. Marker in f. indicates 10μ.



(a) (b)

(c) (d)

Fig. 2 - Concentration of liquid bismuth at a grain boundary in annealed copper. Bismuth is sandwiched between the foil and a thin silicon monoxide film. Dissolution and thinning of the foil occurred at T in d. Marker indicates 10 μ.

sandwiched between the copper foil and the SiO film. When the sample was heated above 271°C, the bismuth melted and agglomerated at grain boundaries as shown in Figure 2. As the accumulation of bismuth increased, dissolution of the copper foil progressed until only a very thin area T remained in the center of the largest pool.

Figure 3 illustrates how liquid bismuth flowed into the thin areas around a crack tip in a single crystal copper foil. The arrow in a. indicates the initiation of fracture. Tension was applied after Figure 3a was taken. The sharply defined black regions around the fracture are composed mainly of liquid bismuth. In c. bismuth has succeeded in flowing around the crack tip T. In f. the crack has propagated beyond the bismuth. The presence of dislocation activity at T indicates that ductile fracture is occurring. This sequence of processes then repeated itself as bismuth again flowed into the tip area T. It can be concluded therefore that liquid bismuth can and does keep up with the tip of a slowly propagating crack. In addition it may aid propagation by dissolving small amounts of copper at the crack tip.

Zinc-Mercury System

In the initial considerations regarding a choice of solid-liquid metal couple, it was concluded that low vapor pressure materials were required. On this basis in situ investigations involving mercury were rejected because of its high vapor pressure at room temperature. It was felt that the mercury would evaporate rapidly in the electron microscope and possibly contaminate it. Subsequent tests showed that rapid evaporation occurred only when the mercury was not in good thermal contact with the solid metal, as for example, when the zinc had oxidized and the oxide layer separated the mercury from the zinc. In cases where mercury wetted the zinc foil it is still felt that slow evaporation must take place, even though it was not observed in the electron microscope in periods of time up to approximately twenty minutes.

Zinc was thinned for electron optical examination by using the same electropolishing solution and methods previously used for copper. A 1% (by weight) solution of $HgNO_3$ in water was used to apply mercury to the zinc foil. A chemical reaction occurred in which the mercury

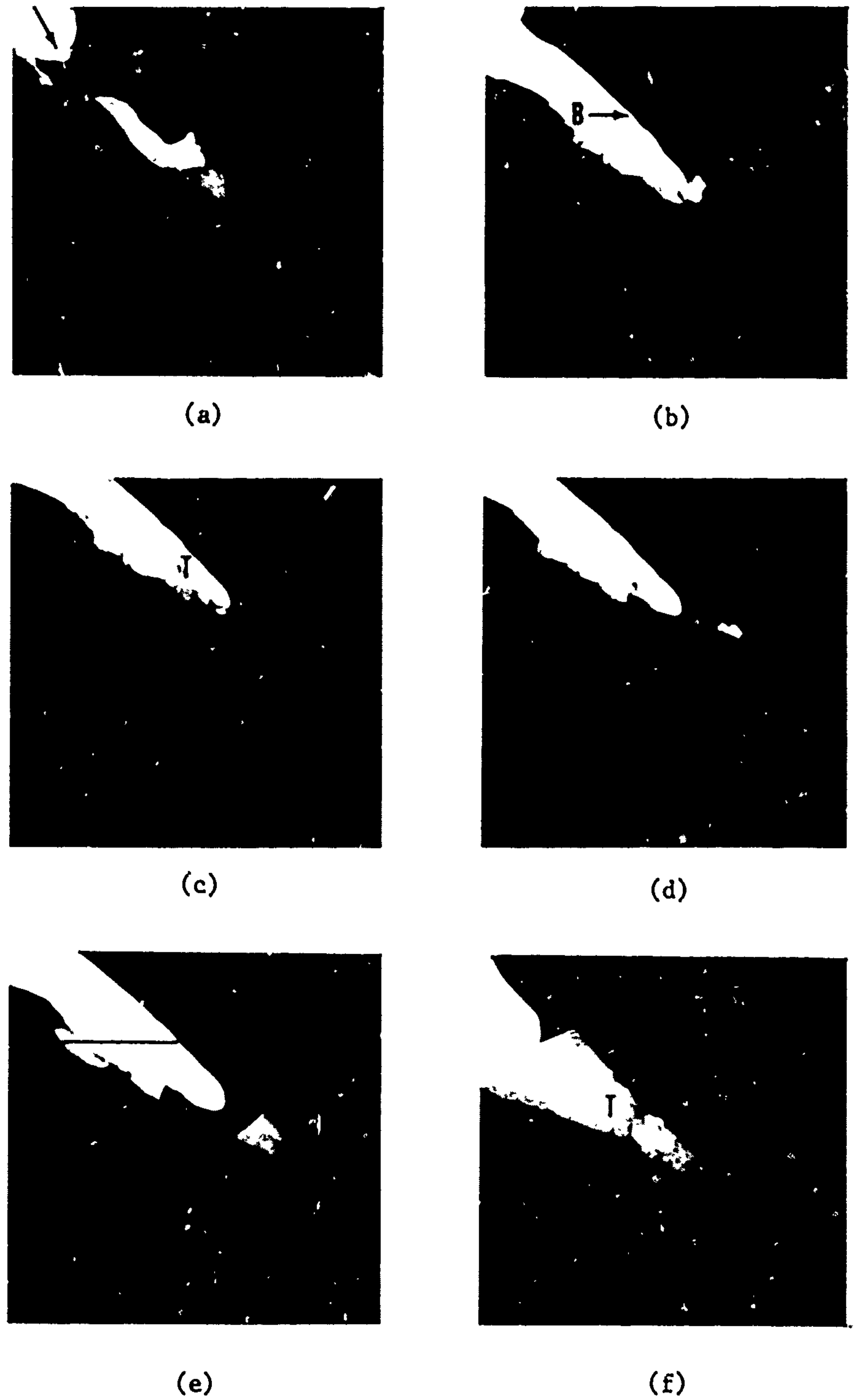


Fig. 3 - An example of liquid bismuth following a crack tip in a single cyrstal copper foil. Marker indicates 1 μ.

in $HgNO_3$ was displaced by zinc leaving free mercury on the surface in intimate contact with the zinc foil. The zinc nitrate which is formed during the reaction is soluble in water and therefore can be washed off. Occasionally, difficulties were experienced with this approach in that the zinc oxidized in air. When this happened, intimate contact between mercury and zinc could not be obtained.

Many of the phenomena observed with the Cu-Bi system were observed also for the Zn-Hg system. The most prominent are the dissolution effects. Mercury dissolves zinc, the amount depending upon time and temperature. Holes may be formed in thin zinc foils as a result of this dissolution.

In addition mercury tended to flow rapidly into the hotter regions of the foil and accumulate there. The rate of flow could be controlled by varying the electron beam current. A high current resulted in rapid flow and could be used to concentrate mercury in the field of view. When the electron beam intensity was decreased, mercury flowed out of the field of view. In this way the flow of mercury over a zinc surface could be studied. This effect is similar to that shown in Figure 1 above for the Cu-Bi system.

It was found that the rate of flow of mercury was much faster along the intersections of grain boundaries and dislocation walls with the surface of the foil than along the surface faces of the grains. Figure 4 illustrates the more rapid flow occurring along grain boundary intersections. It is presumed that the surface tension of the mercury tended to limit the rate of advance of mercury along the grain boundary intersections.

In Figure 5 the preferential flow of mercury parallel to dislocation walls and in the slip direction is shown. The black spots, some of which are labelled S, may be oxide nucleation sites which had formed on the surface of the foil. The flow of mercury could be varied by increasing or decreasing the electron intensity in the field of view. When mercury flowed away from a region it often tended to be held back in a rectangular shaped region bounded by neighboring walls of dislocations. In this way "fingers" of mercury were left behind as the bulk of the mercury receded from a region. See Figures 5 and 6.

(a) (b) (c)

Fig. 4 - Preferential flow of mercury along grain boundary - surface intersections 1 and 2 in zinc. The diffraction pattern in a. refers to the grain G. Marker indicates 10 μ.

(a)

(b)

Fig. 5 - Preferential flow of mercury along dislocation walls D and in slip direction. The arrow in the diffraction pattern of a. indicates a $\langle 11\bar{2}0 \rangle$ direction. E indicates a non-crystallographic dislocation wall. Marker in b indicates 1 μ.

Fig. 6 - Preferential flow of mercury along the face of a zinc foil. The mercury was made to flow in and out of the field of view by changing the electron beam intensity. Marker indicates 1 μ.

The results of the experiments concerned with the flow of mercury over zinc indicated that there was an attractive interaction between mercury and the strained regions around dislocations and grain boundaries in zinc. This conclusion is the same as that which was arrived at in the Cu-Bi system.

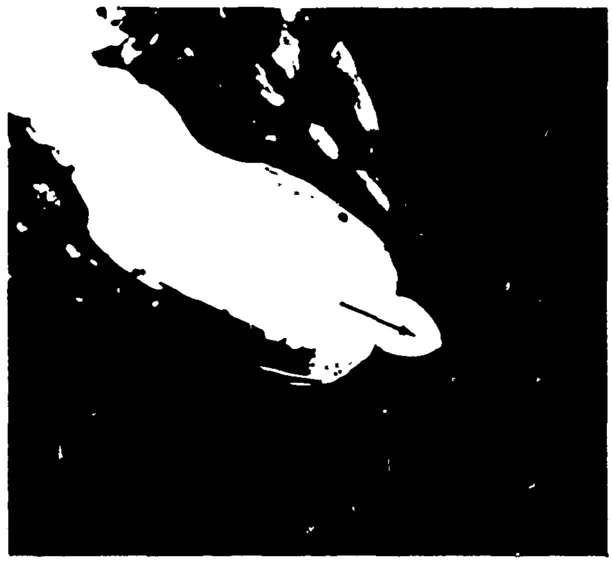
Brittle failure in the Zn-Hg system as observed in the microscope gave results identical to those obtained for the Cu-Bi system. See Figures 6 and 8 of the paper in the Appendix. Failure was again found to be intergranular.

An unusual example of the initiation and propagation of a fracture in zinc wetted by mercury is shown in Figure 7. Observations preceding those in Figure 7 showed that the crack propagated by the formation of a circular depression at the crack tip and the expansion and deformation of this circular depression into a roughly parabolic shape as shown in Figure 7a. Finally another circular depression occurred at the tip of the parabolic crack (indicated by an arrow in Figure 7a.). This circular depression then initiated what appeared to be a brittle fracture. The unusual parabolically shaped initiating crack may be seen in Figure 3a for the case of single crystal copper and bismuth. It is therefore not necessarily related to the presence of a grain boundary. More likely it is related to a dissolution phenomenon whereby dissolution occurs preferentially at a region of high tensile strain.

Our results on the Zn-Hg system may be summarized as follows. Dissolution effects are as pronounced in this system as in the Cu-Bi system. The heating effect of an intense electron beam causes mercury to move into the hotter area. By varying the electron beam current one can cause mercury to flow into or out of the field of view and thereby investigate its flow characteristics over a zinc surface. More rapid flow was observed 1) along grain boundary intersections with the foil surface and 2) along dislocation walls and in the slip direction.

<u>α Brass-Mercury System</u>

Only a few experiments were performed with this system. The brass used was commercial sheet brass. Thinned specimens were produced in an



(a)

(b)

Fig. 7 - Propagation of crack in a zinc foil with mercury present. Arrow in a. indicates initiation of a fracture. In b the fracture has occurred at F. Marker indicates 5 μ.

electropolishing solution identical to the one used for copper specimens. The experiments showed that brass tended to dissolve in mercury. Intergranular brittle failure was observed also when specimens wetted with mercury were pulled in tension in the electron microscope.

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APPENDIX A

DIRECT OBSERVATION OF LIQUID METAL EMBRITTLEMENT IN THE SOLID COPPER-LIQUID BISMUTH SYSTEM*

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Abstract .

An electron microscope investigation of the embrittlement of copper by liquid bismuth has been carried out. Observations were made above the melting point of bismuth (271°C) and at room temperature. A uniform bismuth film was formed by evaporation on a thinned copper foil. When this film melted, it tended to agglomerate (depending on the vacuum conditions and surface preparation prior to deposition) and flow along grain boundaries. The rate of flow increased considerably when a tensile stress was applied. Boundaries in contact with liquid bismuth at temperatures above 271°C were brittle. Boundaries exposed to liquid bismuth for several hours and tested at room temperature were brittle also. The intergranular nature of the embrittlement was verified by transmission electron diffraction and electron microscopy. No evidence for dislocation pile-ups acting to initiate brittle fracture was obtained.

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*This paper was presented at the conference on the Environment - Sensitive Mechanical Behavior of Metals, RIAS, Baltimore, Md., June 1965.

INTRODUCTION

Liquid metal embrittlement phenomena have been investigated for many years and several recent reviews of the field are available.[1,2] While many detailed studies of brittle fracture in liquid-solid metal couples using light-optical techniques have been carried out, no high resolution electron microscope investigations have been reported in the literature. The need for such studies became apparent as a result of well founded theoretical expectations that dislocations and dislocation interactions may play major roles in the initiation and propagation of brittle fracture in normally ductile metals.[1-3] In particular dislocations may form stress concentrations sufficiently strong to initiate fracture. Furthermore, a high resolution examination of the propagation of a brittle fracture may result in some insight into the reasons for the small amount of plastic deformation associated with brittle fractures. Consequently, an electron microscope investigation was undertaken in an attempt to determine the importance of dislocations in the liquid metal embrittlement phenomenon.

The metal couple chosen for this investigation was the solid copper-liquid bismuth system. The reasons for this choice were mainly experimental, such as the requirement for low vapor pressure metals, ease of thinning the solid metal to form electron transparent specimens, and low contamination rates during electron optical examination. Copper and bismuth satisfied the first two requirements. The third could be satisfied by examining the specimens at elevated temperatures. The melting point of bismuth, 271°C, was found to be high enough to inhibit almost completely the formation of contamination films on copper.

Liquid metal embrittlement in this system can be demonstrated readily. If one takes a rod of polycrystalline copper, dips it into liquid bismuth, and bends it back and forth several times, brittle failure will occur after a few bends. However, few investigations of the occurrence of the phenomenon in this particular system have been reported.[1, 4-6]

There are two brittle fracture phenomena occurring in the solid copper-liquid bismuth system. Both are grain boundary phenomena in that fracture is intercrystalline. (Intracrystalline brittle fracture has not been observed in this system). One of these phenomena is the brittle fracture of polycrystalline copper in the presence of liquid bismuth. This is the liquid metal embrittlement problem. Morgan[5] showed that single crystal copper is not embrittled by liquid bismuth. The other phenomenon occurs below the melting point of bismuth (271°C) but only after prior exposure of polycrystalline copper to liquid bismuth for very long periods of time at temperatures above 271°C. This latter phenomenon appears to result from a slow diffusion process in which liquid bismuth penetrates into and weakens the grain boundaries.[5] The boundaries remain weak when the specimen is cooled below 271°C. No evidence for the presence of bismuth in the boundaries (other than the fracture behavior) has been reported in the literature.

These two brittle fracture phenomena differ mainly in their kinetics, those of liquid metal embrittlement being by far the faster. A key to relating them may be Morgan's observation that tensile strains tend to increase the kinetics of grain boundary diffusion.[5] Consequently one might view the liquid metal embrittlement problem as a limiting case of the grain boundary diffusion problem.

Some results of diffusion phenomena in the solid copper-liquid bismuth system have been reported.[4,5,7,8] The rate of diffusion of bismuth into solid bulk copper reaches a maximum near 800°C where the solubility of bismuth is approximately 0.01%. At temperatures around 300-400°C, the solubility of bismuth in bulk copper is much less than 0.001%

and can be neglected for all practical purposes.

The diffusion of bismuth into copper grain boundaries, however, may be quite rapid. An optical microscope investigation by Scheil and Schiessl[8] showed that up to 700°C, bismuth penetrated into copper only along grain edges, a grain edge being defined as the line of intersection of three grains. Between 700°C and 1000°C they found that bismuth penetrated grain faces also.

Morgan[5], however, on the basis of room temperature fracture tests, showed that bismuth diffused into the grain boundary faces of copper at temperatures as low as 300°C. No diffusion experiments were carried out below 300°C. The depth of embrittlement was found to vary linearly with the time the boundaries were in contact with liquid bismuth. At 300°C the rate of bismuth penetration was of the order of 0.1μ per minute. Using an optical microscope, however, he was unable to detect the presence of bismuth in the grain faces. This result was identical to that obtained by Scheil and Schiessl[8] and emphasized the need for higher resolution techniques.

In the present investigation electron microscope techniques were applied to study the fracture behavior of copper in the presence of liquid bismuth. In addition to the liquid metal embrittlement problem, the weakening of grain boundaries at room temperature caused by prior application of liquid bismuth was studied. Tensile tests were carried out in the electron microscope at room temperature as well as in a range of temperatures around the melting point of bismuth. It was shown that the dissolution of copper in liquid bismuth was a prominent feature of the fracture process.

EXPERIMENTAL PROCEDURE AND RESULTS

Sample Preparation - Two kinds of experiments were carried out. One set was performed with a tensile holder containing a heatable stage and a tensile mechanism.[9] With this holder the sample could be strained and examined in a range of temperatures between room temperature and temperatures above that of the melting point of bismuth (271°C). Another set of experiments was carried out with a stereo holder at room temperature. This device contained a biaxial tilting mechanism which made possible the achievement of a wider range of foil orientations relative to the electron beam.

The specimens themselves were prepared from 99.999 pct. copper and 99.999 pct. bismuth. The copper was first rolled into foils and then cut to the right shape for the various electron microscope sample holders. The specimens were then annealed in vacuum at 500°C for several hours. This treatment resulted in reasonably small grains (several microns in diameter), which were relatively dislocation-free. A few specimens were annealed at temperatures above 500°C and these had much larger grain sizes.

After being annealed the copper specimens were thinned by electropolishing in order to form electron transparent regions in the foil. The electropolishing solution consisted of 33 pct. orthophosphoric acid, 22 pct. ethanol, and 45 pct. H_2O. If this procedure were reversed, that is, if thinning preceded annealing, then the thin electron transparent regions disappeared by evaporation or surface diffusion, leaving only thick regions ($>$2500Å thick), which could not be used for electron optical investigations.

Bismuth was deposited on the annealed and thinned copper specimens by vacuum evaporation. A tungsten filament was used and the evaporation took place in a residual gas pressure between 10^{-5} and 10^{-4} torr. Various thicknesses of bismuth films were used ranging from 100 to 200Å (calculated).

When the copper-bismuth specimens were heated, the bismuth film melted and tended to agglomerate into islands on the copper surface. The tendency of thick bismuth films to "dewet" from copper (even when a flux was present) had been noted previously by Hucke et al[6]. These workers were able to get consistent fracture data only after immersing thin samples in a container of liquid bismuth and $ZnCl_2$ flux.

Not only was island agglomeration observed, but also the liquid bismuth tended to flow first towards the intersection of grain boundaries and the copper surface and then along the intersection. This action resulted in very thick bismuth "channels" lying on the grain boundary-surface intersection, where no doubt also enhanced dissolution of copper in liquid bismuth occurred. Earlier work on the zinc-mercury system showed similar preferential attraction to and flow along subboundaries[10] and twins.[10,11]

An attempt to improve the "wetting" characteristics of the liquid bismuth film using better vacuum techniques and cleaner copper surfaces was made. A thinned copper foil was baked at 380°C in a residual gas pressure of about 10^{-6} torr. It was then cooled to room temperature and a bismuth film was deposited on it. Some improvement in adhesion was noted. Nevertheless the tendency for bismuth to concentrate preferentially at various regions of the copper surface was still present. This concentrating effect was again most noticeable where grain boundaries intersected the surface of the copper foil. Finally, no differences in fracture behavior between specimens prepared by the two methods were observed. Consequently, the methods of specimen preparation described in the earlier paragraphs of this section were used throughout this study because of their convenience.

Observations with Specimens at Room Temperature - Copper-bismuth specimens were heated in vacuum to 325°C and kept there several hours before cooling to room temperature. Electron microscope examination of these films at room temperature showed that the liquid bismuth films did not react with intrinsic stacking faults or twins. Fig. 1 shows an intrinsic stacking fault, identified by the analysis of Art et al.[12] It is clear from the figure that the originally uniform film agglomerated upon melting into islands (such as the one at B) and that no bismuth, detectable by mass contrast, is present either in the fault or along the intersection of the fault and the surface. Diffraction contrast experiments gave negative results also. Similarly, twins did not appear to react with liquid bismuth. However, these observations do not imply that bismuth, in very dilute, undetectable concentrations, could not be present in fault or twin planes or at the intersection between such planes and the surface. Nevertheless, it may be concluded that any interaction, if it exists at all, must be small.

On the other hand the tendency for liquid bismuth to etch the copper foil was very strong. Thinned specimens of copper on which thick bismuth films had been evaporated tended to lose the thin electron transparent regions when they were heated above 271°C. Presumably the liquid bismuth dissolved the thinned regions. Fig. 2 is an example of a less severe case (thin bismuth film) in which a hole had been etched in the copper foil. The hole is covered by a thin cuprous oxide layer and the solid black regions are mainly bismuth.

The most prominent and perhaps most important phenomenon that occurred when the bismuth film melted was the concentration at and flow along the intersection of grain boundaries and the surface of the foil. Figs. 3-5 are examples. The point of emergence of a grain edge, defined as the line of intersection of three grains, is shown in Fig. 3. Bismuth has flowed along the grain boundaries at f and h. Region d appears to have been partially depleted of bismuth and it seems probable that some of the bismuth which had been there flowed along the grain boundary at f. Note that little, if any, bismuth flowed down the boundary at g, suggesting that the orientation difference across a boundary may influence the rate of flow of bismuth along it.

In Figs. 4 and 5 liquid bismuth tended to concentrate preferentially at the point of emergence of grain edges. Two such points are shown in Fig. 4, where also considerable flow along the grain boundaries at g has occurred. In Fig. 5 the bismuth agglomerated at the point of emergence of the grain edge and did not spread along the boundaries to any appreciable extent.

Copper specimens coated with bismuth layers 200Å thick and heated to 325°C were brittle when tested by bending at room temperature. An example is shown in Fig. 6. All brittle fractures were intergranular, as determined in many cases by electron diffraction patterns taken from opposite sides of the crack. Moreover, fracture was not necessarily initiated in the thinnest areas of the foil but could start some tens of microns away and propagate into areas still farther away. The fracture surfaces were flat and indicated that very little plastic deformation occurred near the crack edge. For comparison see Fig. 7, which shows a ductile fracture. In this case the crack edges are bounded by jagged, torn regions of varying thickness, indicating that large amounts of plastic deformation had occurred.

Several high resolution electron microscope examinations of brittle boundaries were made prior to the bend tests in an attempt to find some distinguishing characteristics in them. None were found.

Observations with Specimens at Temperatures above 271°C - In these experiments specimens were examined in the electron microscope at temperatures slightly above the melting point of bismuth (271°C) and under varying amounts of tensile stress. As mentioned earlier, when the bismuth film melted, it tended to agglomerate and flow along the intersections of grain boundaries and the surface of the foil. Moreover dissolution of the foil by the liquid bismuth occurred preferentially where large concentrations of bismuth occurred. Holes formed in the foil in times of the order of several minutes in regions where the foil was approximately 1500Å thick.

When tension was applied to the specimen, intergranular fracture occurred. The extreme weakness of large angle grain boundaries in the presence of liquid bismuth (relative to the bulk material) was illustrated by the fact that boundaries far from the thinned areas sometimes failed first. Such failures occurred in foils which had been annealed at high temperatures (800-900°C) in order to produce a very large average grain size. As a result intergranular failure often occurred in regions which were many times thicker than those surrounding the hole produced by electropolishing. It may be concluded that grain boundaries of copper in the presence of liquid bismuth are much weaker than the bulk material, in agreement with earlier fracture studies.[1,6]

Fig. 8 is an example of liquid bismuth embrittlement of annealed copper. Stress was applied in the intervals between the times when the micrographs were taken. Fracture occurred in a jerky manner. In all cases where electron diffraction measurements could be made fracture was found to occur along large angle grain boundaries. The fact that many fracture surfaces tended to be straight was further evidence for its intergranular nature.

High resolution micrographs showed that there were no large electron transparent regions near the fracture surfaces.

A very common type of "fracture" is illustrated in Fig. 9. Here two cracks (white areas) were moving towards each other under the influence of a tensile stress. Crack propagation appeared to occur as though a very viscous material were being pulled apart. The viscous material is most likely a liquid or semi-liquid bismuth-copper alloy.

A further example of intergranular embrittlement of copper by liquid bismuth is shown in Fig. 10. The electron transparent area was quite extensive in this sample. In (a) liquid bismuth has flowed along the intersection of grain boundary G and the surface of the foil. A slight tensile stress caused the fracture shown in (b). Further stress caused the crack to propagate as shown in (c). In (d) an enlarged view of area R of (c) is shown in which a high dislocation density is evident. It is, however, not known at what stage of the fracture process these dislocations were formed.

Fig. 11 illustrates the preferential weakening of grain boundaries and a grain edge at E. When a slight tension was applied, liquid bismuth flowed slowly towards E along the grain boundary intersection labelled 1. Under increased tension the bismuth reached E and then with extremely high velocity flowed out along boundary 2. The black band along 1 and 2 in (b) is due to the mass contrast of the liquid bismuth. Finally, under more tension, a crack opened up at F. It may be noted that bismuth was beginning to flow down boundary 3 in (b) and more so in (c).

<u>Observations with Single Crystal Specimens</u> - Several single crystal copper specimens were examined. In each case approximately 150-200Å of bismuth was deposited on one side of the thinned copper foil. The samples were placed in the tensile holder mentioned earlier[9] and then heated until

the bismuth film melted. Agglomeration of bismuth was observed to occur in the same manner as with polycrystals.

When a tensile stress was applied to a single crystal foil in the presence of molten bismuth, ductile fracture resulted. In addition, dissolution of copper by liquid bismuth occurred at the edges of the crack leaving thick, blunt walls which were impenetrable to 100 kv electrons. When a drop of liquid bismuth remained in one region for many minutes, holes were formed in the foil. Again, these holes resulted from the dissolution of copper by liquid bismuth. In two cases thinned copper foils which had been exposed to a liquid bismuth film for ten minutes were cooled to room temperature and deformed. Ductile fracture resulted. It may be concluded that single crystal copper in the presence of liquid bismuth deforms in a ductile manner, a result obtained earlier by Morgan.[5]

DISCUSSION

Essentially three types of fracture were observed in this investigation: ductile fracture, exemplified by Fig. 7; dissolution effects, Figs. 2-5, 9-11; and brittle fracture, Figs. 6,8. The type of fracture observed may not always be clearly identified. For example, when a tensile stress is applied rapidly to a polycrystalline copper sample in contact with liquid bismuth, brittle fracture occurs. However, when the strain rate is decreased, dissolution of copper in liquid bismuth (to an extent determined by temperature) becomes an important feature of the fracture process. Liquid bismuth is attracted preferentially to the grain boundaries and flows along them in a manner resembling capillary action. When the boundaries are under strain, the flow of liquid bismuth along them and away from the liquid bismuth source is considerably enhanced. Dissolution then occurs preferentially at the intersections of grain boundaries and grain edges with the surface of the foil.

For slow strain rates, dissolution effects may mask both ductile and brittle failure. In fact hole formation and subsequent fracture were observed to occur in both polycrystals and single crystals of copper solely as a result of the dissolution of copper in liquid bismuth. Dissolution effects tended to round off fracture surfaces by dissolving thin regions of the foil. By contrast, brittle fracture surfaces tended to be planar because they lay along grain boundaries.

In order to eliminate dissolution phenomena one could in principle pre-saturate the bismuth so that at a particular temperature, dissolution would not occur. However, in practice it is virtually impossible to maintain the temperature constant. Slight changes in temperature would cause dissolution or precipitation[13] effects. In addition deforming the sample would cause localized heating, which also would result in localized dissolution. Since the brittle fracture phenomenon is in all probability a surface effect, a small amount of dissolution would undoubtedly influence it. A further point is that during electron microscope examination, the electron beam produces a substantial heating effect in the specimen. Consequently the local temperature in the area being examined is difficult to control to within several degrees centigrade. It is evident, therefore, that dissolution phenomena cannot be completely eliminated by presaturating the liquid metal.

Earlier investigations by other workers of the solid copper-liquid bismuth system illustrated the importance of grain boundary diffusion phenomena in intergranular failure at room temperature.[1,5] The present investigation showed that liquid bismuth preferentially agglomerated along the intersection of large angle grain boundaries and the surface. Once at such an intersection the liquid bismuth tended to flow along it. Moreover the agglomeration of liquid bismuth resulted in localized dissolution of the copper foil. Dissolution, even in the absence of stress, resulted in local fracture. Consequently it appears that intergranular fracture is initiated in this system by preferential dissolution occurring where large angle grain boundaries intersect the surface. No evidence for a dislocation mechanism was obtained and it is felt that such a postulate is unnecessary in this system.

Crack propagation could be observed only when it was slow enough to follow in the electron microscope. In such cases the presence of liquid bismuth in the area around the crack tip tended to obscure the observations. Grain boundary diffusion phenomena became important also. As mentioned earlier the rate of diffusion of bismuth into a grain boundary of copper at $300^{\circ}C$ is about 0.1μ/min.[5] Consequently the time required for bismuth to diffuse through an electron transparent region 2000Å thick is approximately two minutes, a time comparable to the time of observation. In much thicker specimens this type of diffusion is not important since brittle fracture during deformation can occur almost immediately after the sample is immersed in liquid bismuth. However some other kind of diffusion phenomenon[14], occurring during the fracture process, cannot be ruled out because much evidence exists which indicates that the liquid metal must be at the fracture tip in order for the crack to propagate.[1,2]

With two samples an apparent interaction was observed between dislocations moving away from a fracture tip into the sample and liquid bismuth present at the tip. As individual dislocations were nucleated and subsequently moved away from the crack tip, bismuth was pulled along with them until the bismuth reservoir deformed so as to have a pointed surface of very short radius with its apex at the dislocation. When the surface tension forces of the liquid bismuth finally overcame the apparent attraction of the dislocation, the pointed liquid surface snapped back into the reservoir. At the same time the dislocation, now freed from the liquid, moved rapidly towards thicker regions of the sample. The existence of similar attractive forces between dislocations and adsorbed liquids has been demonstrated earlier in other systems.[15] From these observations it is inferred that liquid bismuth can inhibit dislocation nucleation and subsequent motion in copper.[16] Consequently plastic deformation at a fracture surface would be made more difficult thus leading to more brittle-like behavior.

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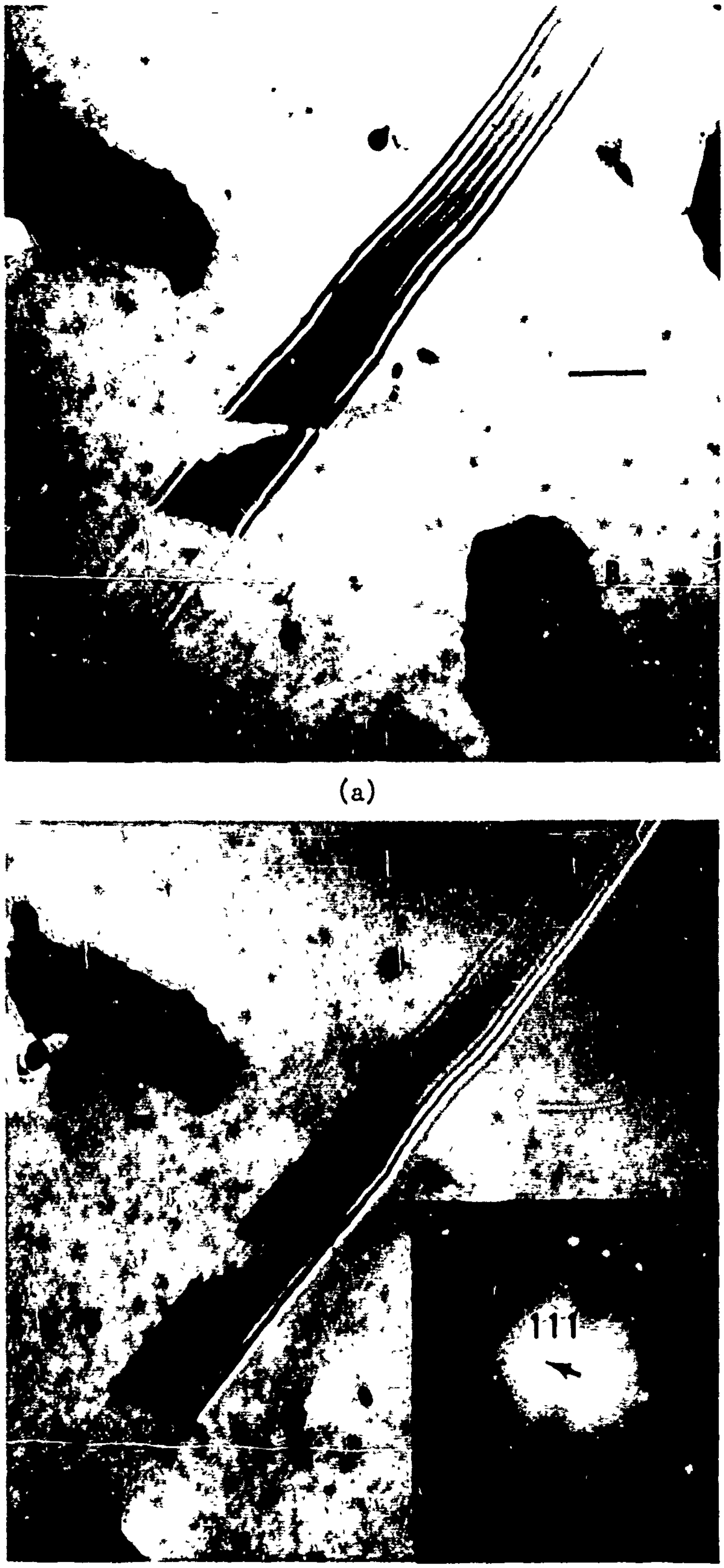


(a)

(b)

Fig. 1 - Intrinsic Stacking Fault in a Copper Foil (a) Birght Field, (b) Dark Field Taken with 111 Reflection. See insert. The Marker Incicates 0.2μ.

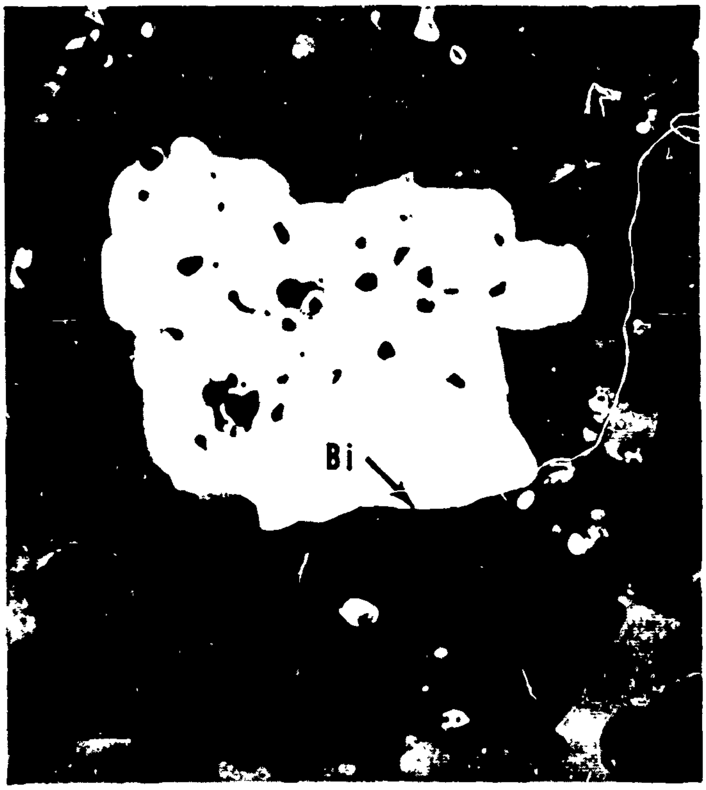


Fig. 2 - Effect of Liquid Bismuth on a Copper Foil. The Bismuth (black regions) has Etched a Hole in the Foil. Marker Indicates 1.0μ.

Fig. 3 - Effect of Liquid Bismuth on a Copper Foil. When the Bismuth Melted, it Agglomerated at and Flowed Along the Grain Boundaries f and h. d Indicates the Source of Some of the Bismuth which Flowed Along f. Marker Indicates 1.0μ.

Fig. 4 - Effect of Liquid Bismuth on a Copper Foil. Concentration of Bismuth at and Flow Along Grain Boundaries g. The Micrograph' Shows Preferential Concentration at the Points of Emergence of Two Grain Edges. Marker Indicates 1.0μ.

Fig. 5 - Copper Foil Showing the Point of Emergence of a Grain Edge b and Grain Boundaries f, g, and h. Liquid Bismuth Segregated at the Intersection of the Grain Edge and the Surface of the Foil. Marker Indicates 0.2μ.

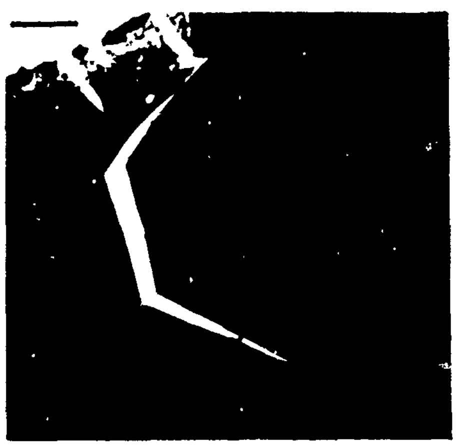


Fig. 6 - Brittle Fracture in a Copper Foil Annealed at 500°C. A 200Å Bismuth Film was Deposited on the Foil. The Combination was then Heated to 325°C for two hours. The Sample was Bent at room Temperature. Marker Indicates 5.0μ.

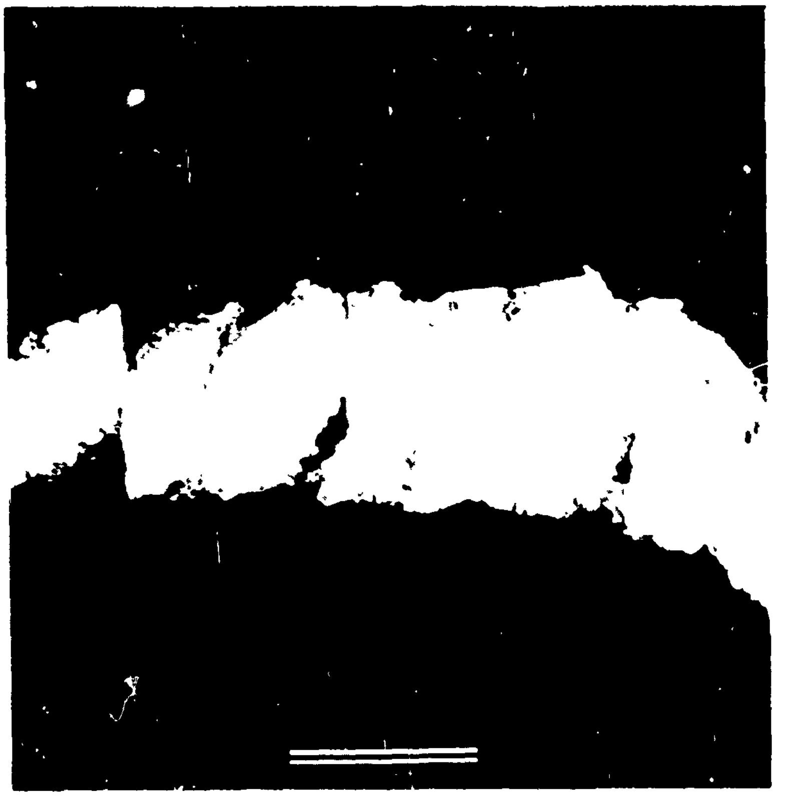
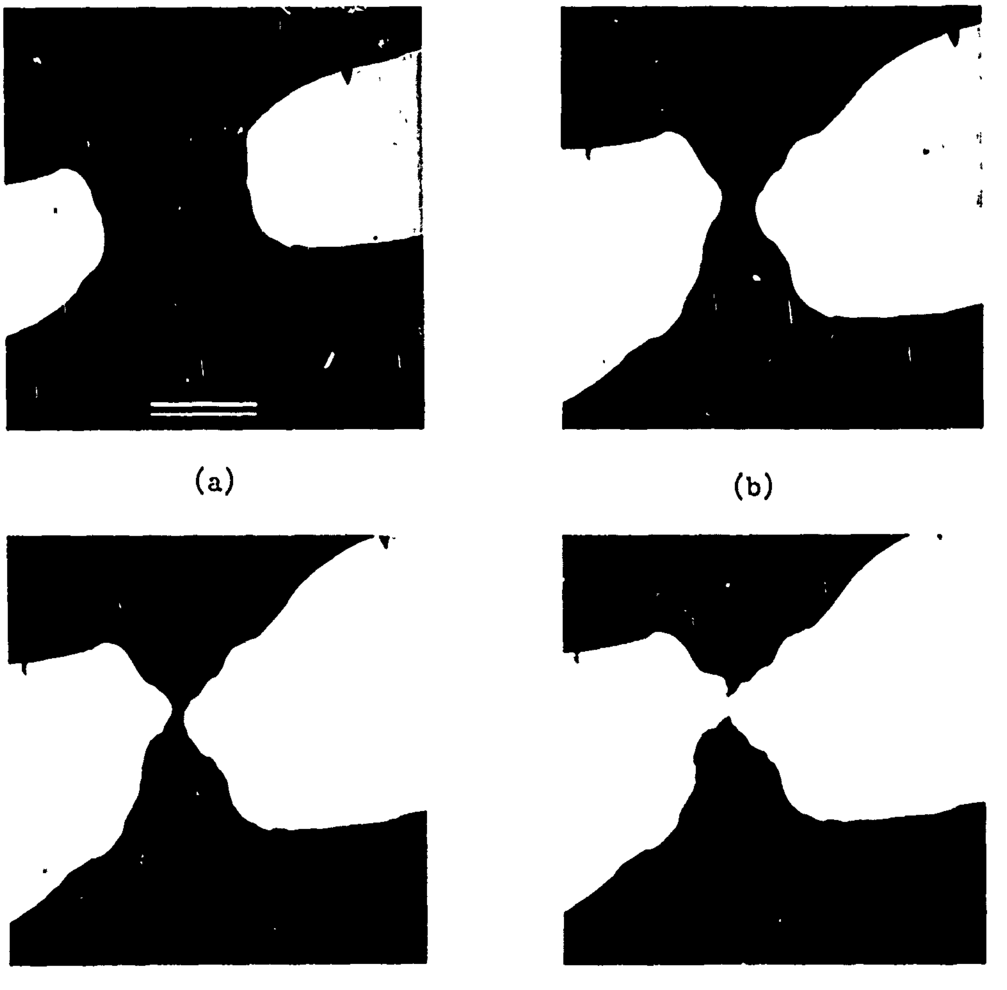


Fig. 7 - Ductile Fracture in a Copper Foil Annealed at 500°C. The Foil was Deformed at Room Temperature. Marker Indicates 1.0μ.

(a) (b) (c) (e)

(d)

Fig. 8 - Brittle Fracture in a Copper Foil Annealed at 900°C Caused by a Liquid Bismuth Film Originally 150Å Thick. The Hole H was Formed During the Thinning Process. The Sample was Successively Deformed in the Tensile Holder at a Temperature Above 271°C in the Order a, b, c, and d. Marker Indicates 10μ.



(a) (b) (c) (d)

Fig. 9 - Progressive Motion of a Fracture After Successive Deformations in the Tensile Holder at a Temperature Above 271°C. The Copper Foil had been Annealed Previously at 1000°C. The Bismuth Film was Originally 200Å Thick. Marker Indicates 2.0μ.

(a) (b) (c)

(d)

Fig. 10 - Flow of Liquid Bismuth and Fracture Along the Grain Boundary G in a Foil Annealed at 950°C and Successively Deformed in the Tensile Holder. Marker for a, b, and c Indicates 5.0μ. Region R is Enlarged in d Where the Marker Indicates 1.0μ. Bismuth Agglomerations r, s, and t are for Reference to the Region to the Left of R in C.

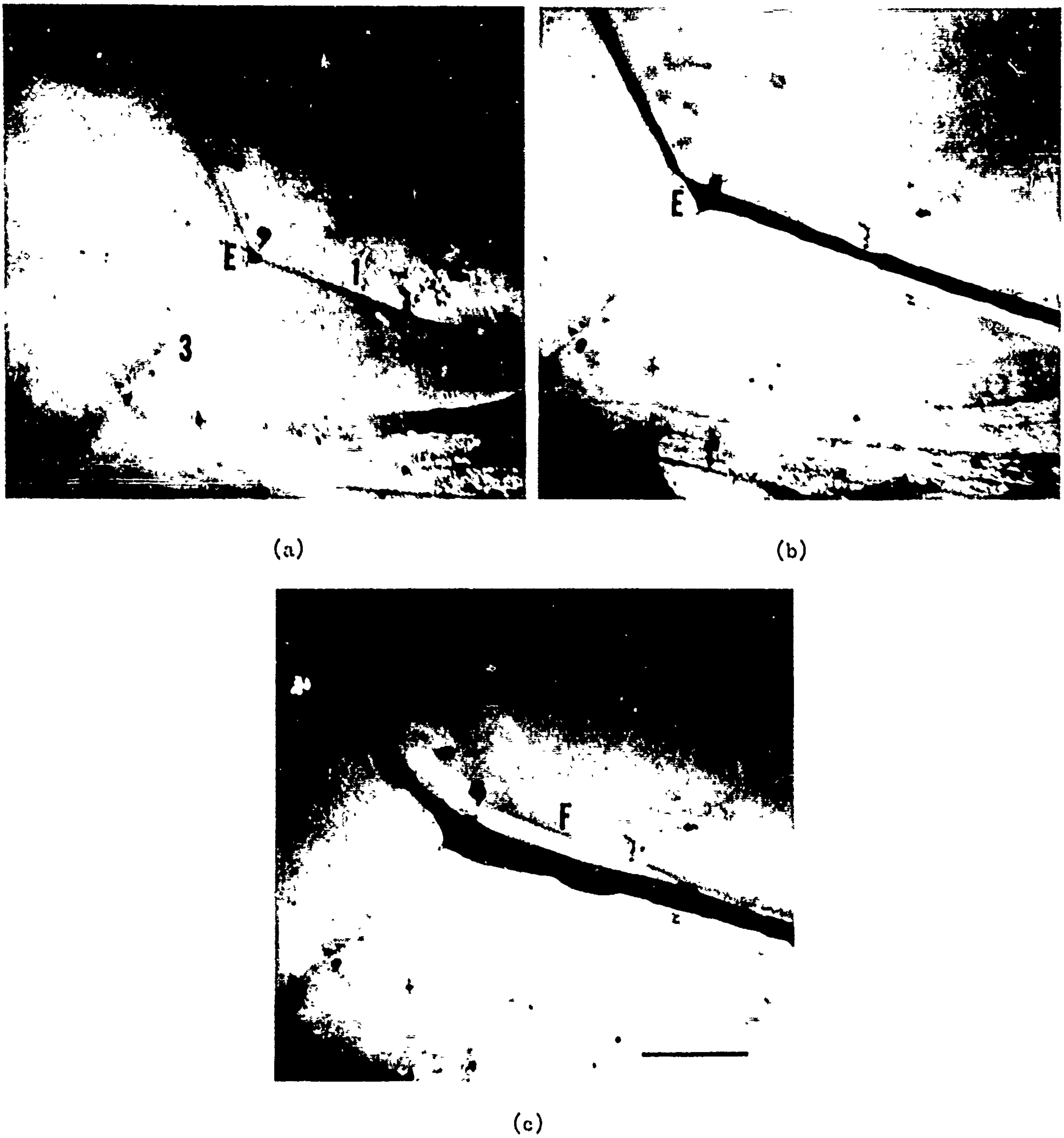


Fig. 11 - The Emergence of a Grain Edge at E in a Copper Foil Annealed at 1025°C and Subjected to Successive Tensile Deformations at a Temperature Above 271°C. The Original Bismuth Film was 200Å Thick. Liequid Bismuth Flowed along the Grain Boundary at 1 to E and then along 2. The Black Region is Liquid Bismuth. Fracture has Occurred at F. Marker Indicates 5.0μ.

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13. ABSTRACT

An electron microscope investigation of the embrittlement of copper by liquid bismuth has been carried out. Observations were made above the melting point of bismuth (271°C) and at room temperature. A uniform bismuth film was formed by evaporation on a thinned copper foil. When this film melted, it tended to agglomerate (depending on the vacuum conditions and surface preparation prior to deposition) and flow along grain boundaries. The rate of flow increased considerably when a tensile stress was applied. Boundaries in contact with liquid bismuth at temperatures above 271°C were brittle. Boundaries exposed to liquid bismuth for several hours and tested at room temperature were brittle also. The intergranular nature of the embrittlement was verified by transmission electron diffraction and electron microscopy. No evidence for dislocation pile-ups acting to initiate brittle fracture was obtained.

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